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Modeling and optimization of diffusive layers in potentiometric and amperometric electrochemical gas sensors

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Abstract

A physicochemical model of the behavior of electrochemical gas sensors based in a solid-state ion conducting electrolyte is presented and verified. The model focuses on air-referenced planar sensors with a porous, diffusive layer covering one of the electrodes. By assuming hypotheses of ergodicity, ordinary diffusion, near-equilibrium situation, high catalytic activity and steady-state mass conservation in the system layer/electrode/electrolyte/electrode, the model describes the current-voltage characteristics both in steady-state as in transient conditions. Numerical simulations, including finite element modelling, are used for obtaining the model preditions for I(V), I(t) and V(t) responses in front of binary O_2-N_2 mixtures and multi-component mixtures. The model is validated with our own-designed sensors with different diffusion layers.

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Keywords: exhaust gas sensors; YSZ; porous layer; diffusion.

1. Introduction

We have previously developed some basic physicochemical models on the behavior of solid-state electrochemical-based oxygen sensors attending to the diffusivity of their porous layers [1] and phenomenological descriptions on the diffusive filter-effect of these layers in multi-component gas mixtures [2-3]. We propose a generalization of the previous models to multi-component gases both in steady-state and transient conditions in potentiometric and amperometric measurements. The objective of this work is to model, verify and optimize the behavior of conventional solid-state electrochemical gas sensors in terms of the diffusion layer covering one of their catalytic electrodes.

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2. Experimental

Several ceramic-based sensors with the structure (diffusive layer) / electrode / electrolyte / electrode have been designed. Fig.1 shows an schematic view of the prepared samples. Electrodes areade of platinum with a 30%wt. loading of Y_2O_3-doped ZrO_2 (yttria-stabilized zirconia, YSZ). The electrolyte is a solid-state O^{2-} ion conducting ceramic (YSZ). Both electrodes are exposed to the same atmosphere, but one of them is covered by a porous, diffusive material. Details on monolithic ceramic technology for the preparation of this kind of sensors, including tape casting, screen printing and ceramics cofiring, can be found elsewhere [4]. Sensors with this structure are very usual in the context of oxygen and exhaust gas detection. When exposed to a multi-component gas mixture at high temperatures (between ~400ºC and 800ºC), these sensors provide an equilibrium Nernst voltage in terms of the ratio of oxygen partial pressures between each electrode.

Several families of sensors have been prepared by introducing differences in the diffusivity of porous layers. The layers were initially made of Al_2O_3 and a sacrificial material. As the ceramic process included ceramic firing at 1450ºC, the sacrificial material was burnt and pores were generated. Table 1 indicates the kind of sacrificial material (conventional graphite or carbon nanofibers) and its concentration in the layers. This has led to a set of almost identical sensors but with different expected pores size and density (i.e. different diffusivity) in their porous layers covering one of the electrodes. Fig.2 shows an example of two very different porous layers, with different morphologies.

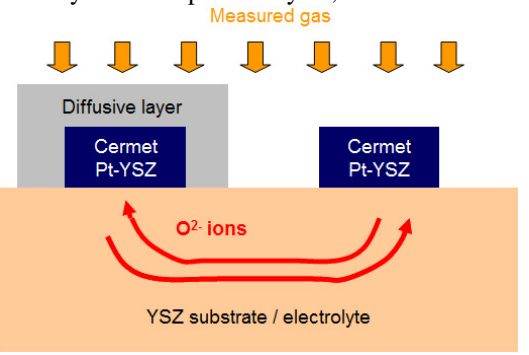

Fig.1. Schematic cross-sectional view of the designed structure. Both electrodes were exposed to the same atmosphere. However, the steady-state gas composition in the nearby of the three phase boundary reaction sites of each electrode was not necessarily the same, as one of the was covered by a diffusive layer.

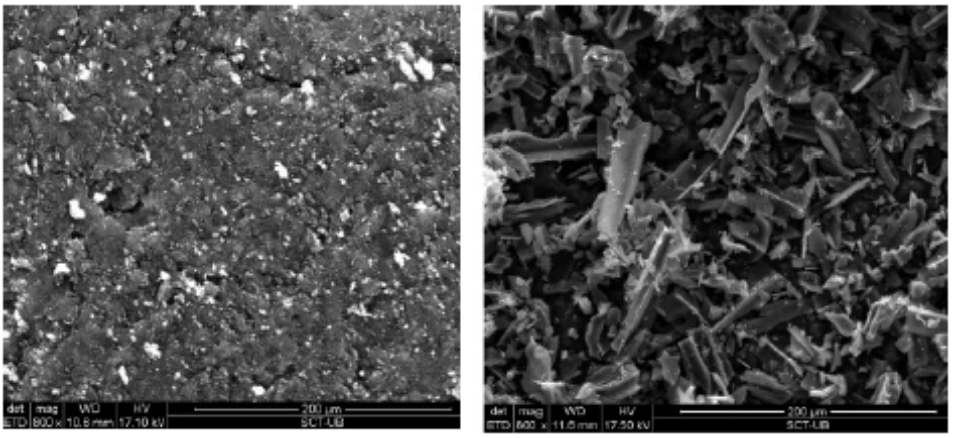

Fig.2. Porous YSZ, with two very different morphologies of diffusion layers: (left) pores generated by carbon nanofibers, (right) pores generated by graphite micropowders.

Table 1. List of groups of sensors with the differences between their diffusive layers.

Sensors family	Pore density	Sacrificial material	Qualitative behavior
A	40%	Graphite powder <100µm	Almost 'transparent' layer
B	40%	Graphite powder <20µm	High molecular diffusivity
C	20%	Graphite powder <20µm	High molecular diffusivity
D	5%	Graphite powder <20µm	Low diffusivity
E	1%	Graphite powder <20µm	Low diffusivity
F	1%	Carbon nanofibers	Extremely low diffusivity

Sensors were allocated in a synthetic gas testing chamber at a controlled temperature of 700ºC to different O_2-N_2 binary gas mixtures and O_2-N_2-CO mixtures. Their temporary open circuit voltage was registered while exposing to these mixtures, in order to calculate their equilibrium response and their transient behavior as well. Sensors were measured as amperometric sensors as well, by carrying out different cyclic voltammetries.

3. Results

Fig.3 shows different behaviors for some of the prepared gas sensors families. The positive voltage is for the electrode which was not coverd by the diffusive layer (i.e. directly exposed to the measured gas). Two main qualitative differences can be pointed. First, some groups of sensors (families A and C, in the case of Fig.3) showed a stationary voltage which was, in average, zero (sensor A) or almost zero (sensor C) whereas other sensors provided a nonzero steady state voltage. Second, a negative transient voltage was detected in the case of sensors A, D and F, but not in sensors of the C-family. The duration of the transient behavior seemed to correlate with the magnitude of the steady state voltage.

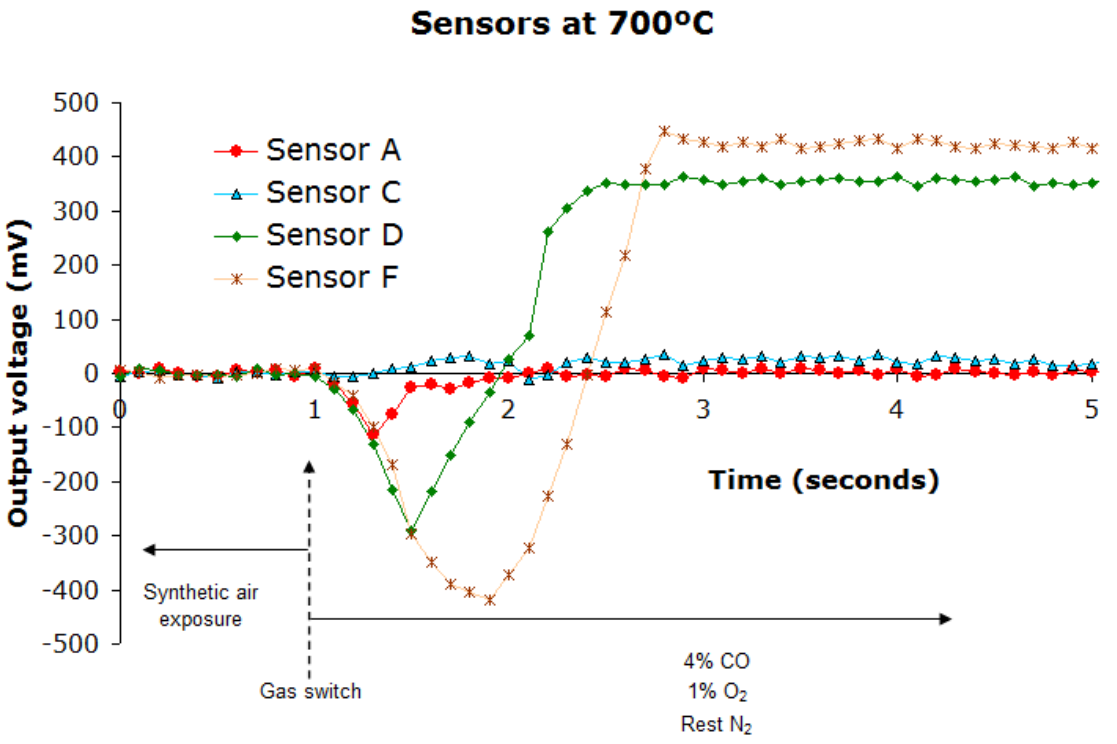

Fig.3. Example of the behavior of sensors belonging to different families.

The observed behaviors can be discussed by separating the electrochemical phenomena in the Nernst Pt/YSZ/Pt cell from the diffusive behavior in the porous layer covering one of the electrodes. Certainly, if the two electrodes are exposed to the same atmosphere, its equilibrium open circuit voltage should be zero as they are made of the same material (cermet Pt-YSZ) and no mixed potential effects can be taken into account. This is the case of sensor family A, with a 40% porosity in the diffusive layer. A layer with a so high porosity lets the diffusion through the electrodes with almost no blocking effects.

Multi-component gas mixtures may lead to different diffusivities for each molecular species. As the second gas mixture contains carbon monoxide, oxygen and nitrogen, it is possible that the respective molecular partial pressure in the bulk gas is different from the local partial pressure of each gas species in the nearby of the interface electrode-electrolyte, as molecules diffuse through the porous layer. This effect should be more evident as increasing the density of the porous layer (i.e. decreasing the layer porosity). This is in accordance with the observed behaviors, as the highest layer density (Sensor family F) leads to the highest open circuit voltage.

4. Conclusions

Sensors with the lowest porosity (1% porosity with carbon nanofibers as the sacrificial material) led to the most sensitive response due to the filtering effect of the diffusive layer before reaching the catalytic electrode. This made the molecular partial pressures in the nearby of the interface electrode-electrolyte different from the partial pressures in the bulk gas.

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